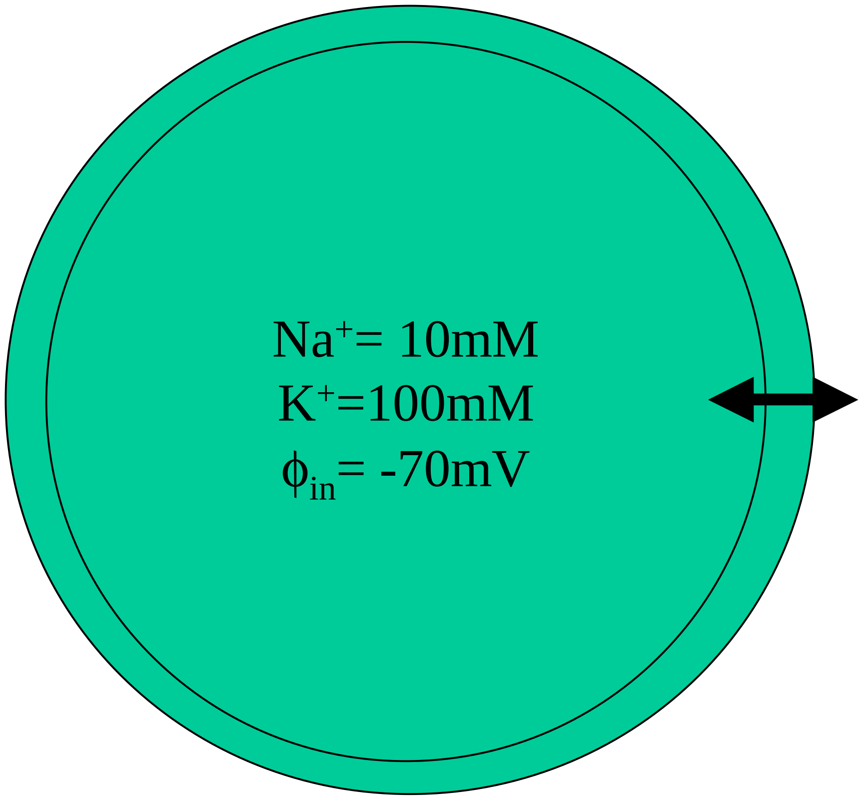
Transport and Forces Thereupon

Membrane Transport

- Electrochemical gradients
- Passive,Facilitates and Active Transport

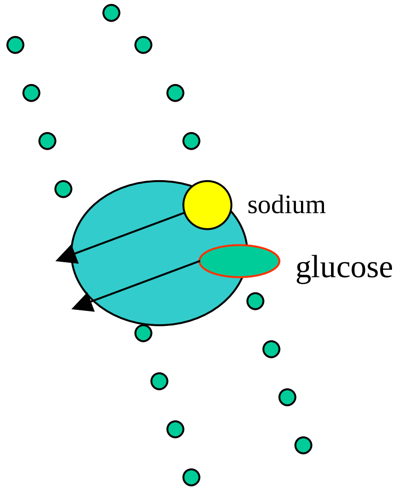
Colligative properties

- Raoult’s and Henry’s Laws
- Boiling point elevation
- Freezing point depression
- Osmotic Pressure



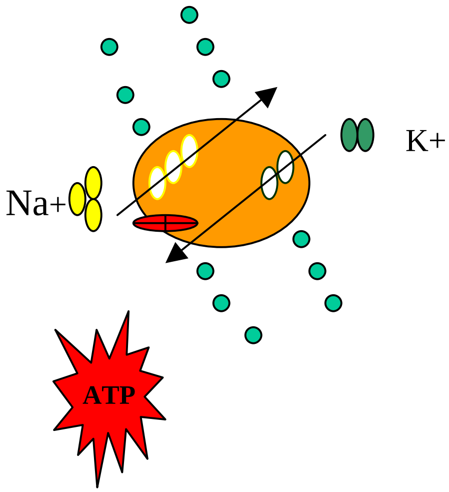
H_2O?

Facilitated Diffusion

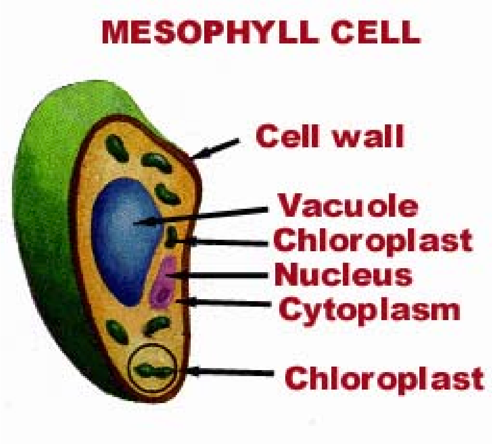


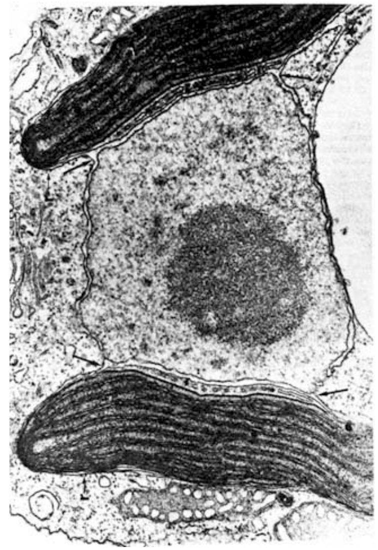
- * utilizes carrier proteins.
- * lacks ATPase activity.
- * energy provided by Na+ passing down its gradient.
- * uses symport transport; moves simultaneously in same direction
- - sodium binds first for conformational change.
- - allowing glucose to bind its receptor site.
- - sodium moves in and releases.
- - at next binding glucose is released form inner side of membrane.

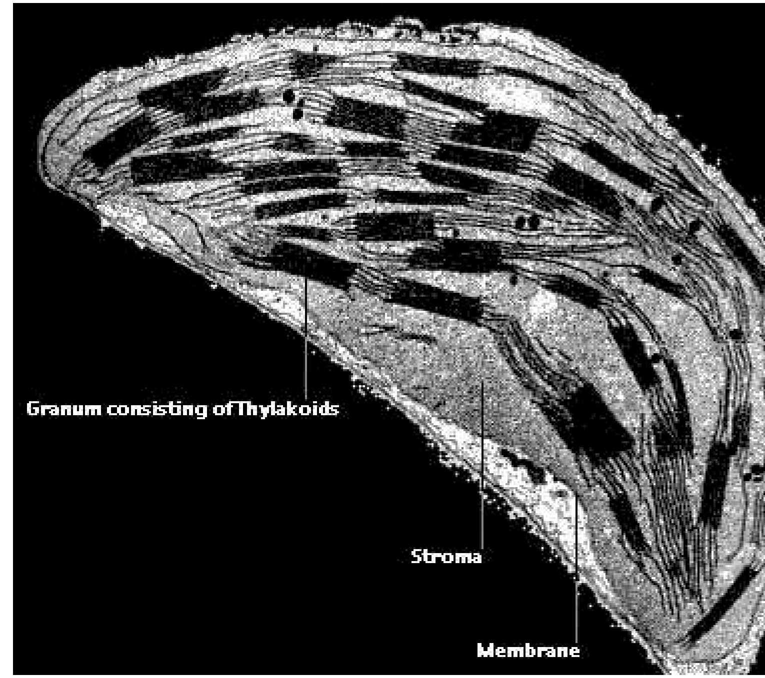
Active Transport

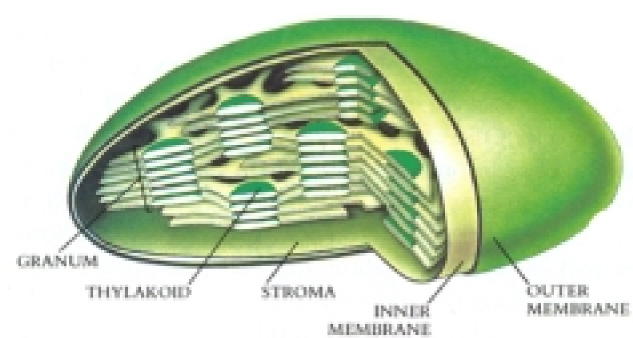


- Utilizes receptor binding
  - 3 Na+ ions bind to inner face with simultaneous ATP bind to carrier.
  - carrier changes shape.
  - attracts 2 K+ ions to outer face binding sites.
  - carrier returns to original shape, releasing K+ ions into cell.
- saturation kinetics
- unidirectional for each substrate
- requires ATP to charge the carrier for transport


MESOPHYLL CELL
Cell wall
Vacuole
Chloroplast
Nucleus
Cytoplasm
Chloroplast



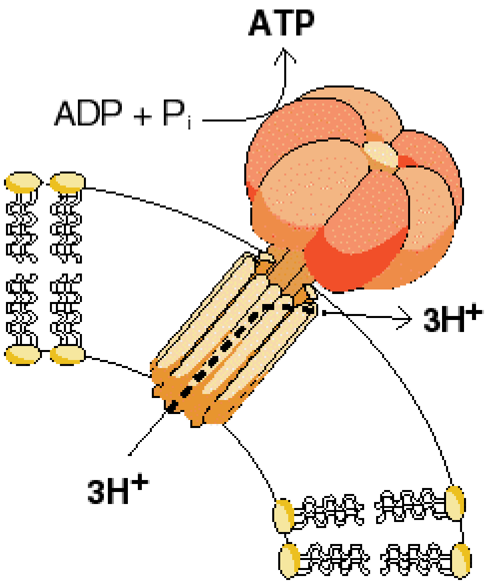

Granum consisting of Thylakoids
Stroma
Membrane


GRANUM
THYLAKOID
STROMA
INNER MEMBRANE
OUTER MEMBRANE

In a mammalian system the flow of ions between compartments is precisely regulated.

1) Cell Volume, pH, Ionic Composition are all controlled within a narrow range
(cell shape and enzymatic activity optimized)
2) Extraction and concentration of metabolic reactants
Excretion of products and toxins
3) Generate ion gradients-- essential for excitability of nerve cells and muscle
Drives formation of ATP

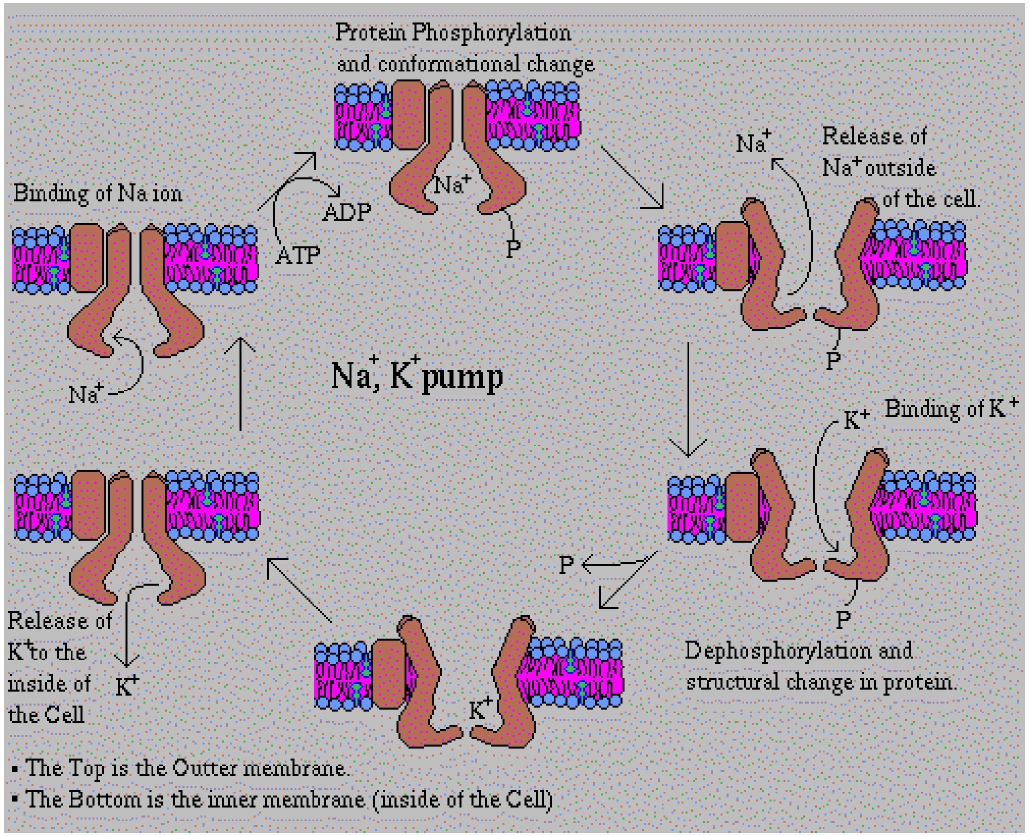
e.g. Membrane bound permeases (LacY, etc.)
Na^+/K^+ ATPases



This is an ATPase that transports protons with or against a gradient to create or burn ATP

Like many other such pumps:

1) The enzyme is coupled to ion transport
2) Depends on Ionic Concentrations
3) Can be inhibited by specific drugs.



100 x/second

The sodium/potassium pump, for example, is inhibited by

1) Cardiotonic steriods
digitonin
oubain
(outside cell)

2) Vanadate (inside cell)

3) Can reverse direction based on ATP/ADP ratios

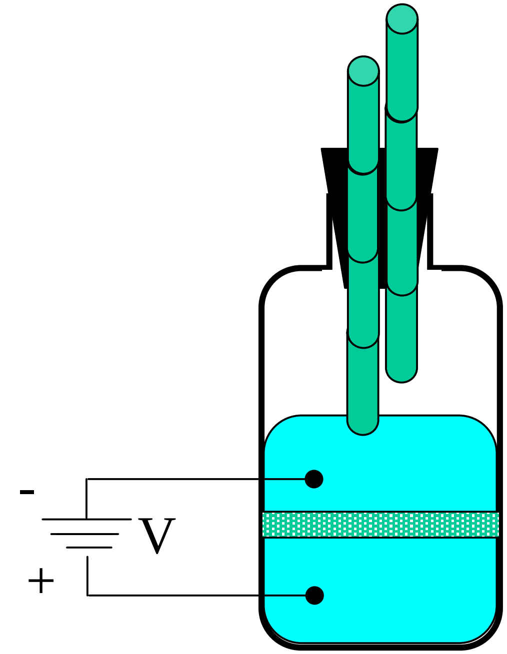
Stoichiometry is such that 3 Na^+ go out and 2 K^+ in per ATP

The Na+-K+-ATPase is a highly-conserved integral membrane protein that is expressed in virtually all cells of higher organisms. As one measure of their importance, it has been estimated that roughly 25% of all cytoplasmic ATP is hydrolyzed by sodium pumps in resting humans. In nerve cells, approximately 70% of the ATP is consumed to fuel sodium pumps.

At equilibrium then, there is an unequal concentration of ions on either side of the membrane!

The chemical potential must be modified to deal with this effect:

$$\Delta\mu = \cancelto{0}{\Delta\mu^\circ} + RT \ln(\mathbf{a}_{ion}(\text{outside})/\mathbf{a}_{ion}(\text{inside}))$$

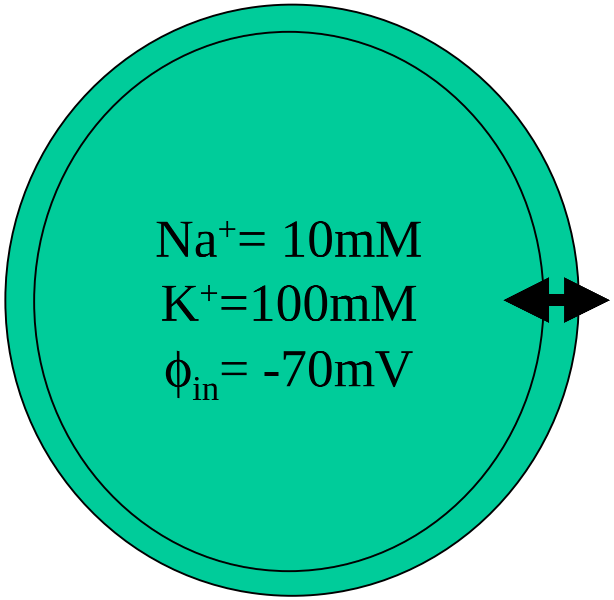


Plus a term indicating the free energy of transfering a charge down a potential gradient:

$$\Delta\mu_{field} = Z\ F\ V = Z\ F\ (\phi_{in} - \phi_{out})$$

So the total $\Delta\mu$ for the equilibrium described is

$$\Delta\mu = RT \ln(\mathbf{a}_{ion}(\text{outside})/\mathbf{a}_{ion}(\text{inside})) + Z\ F\ V$$



Na^+= 140mM
K^+=5mM
ϕ_{out}= 0mV

ΔG(transport of Na+ out) $= RT \ln(\mathbf{a}_{\mathbf{Na+}}(out)/\mathbf{a}_{\mathbf{Na+}}(in)) + \quad Z F V$

$= RT \ln(140/10) + \quad Z F (\phi_{out} - \phi_{in})$

$=(8.3144)(310)*\ln(140/10)+ \quad 1*F*0.07$

$= 13.6$ kJ/mol

(Why is there no $\Delta G°$)

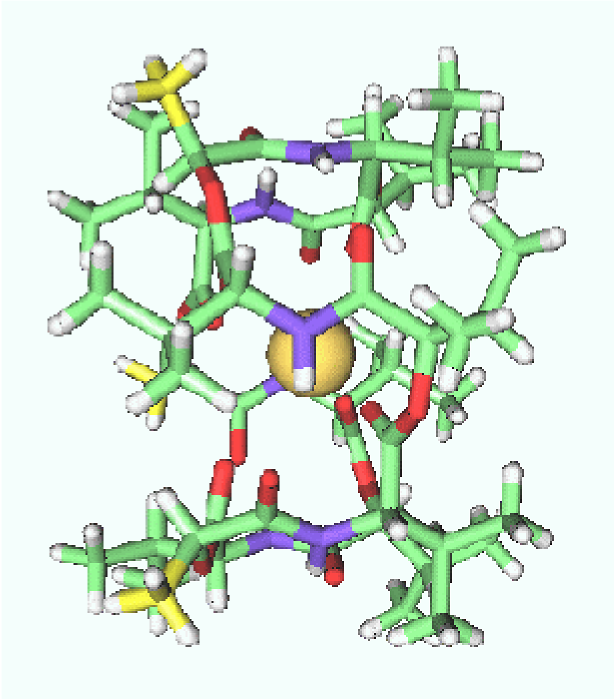
ΔG(transport of K+ in)= 1.0 kJ/mol

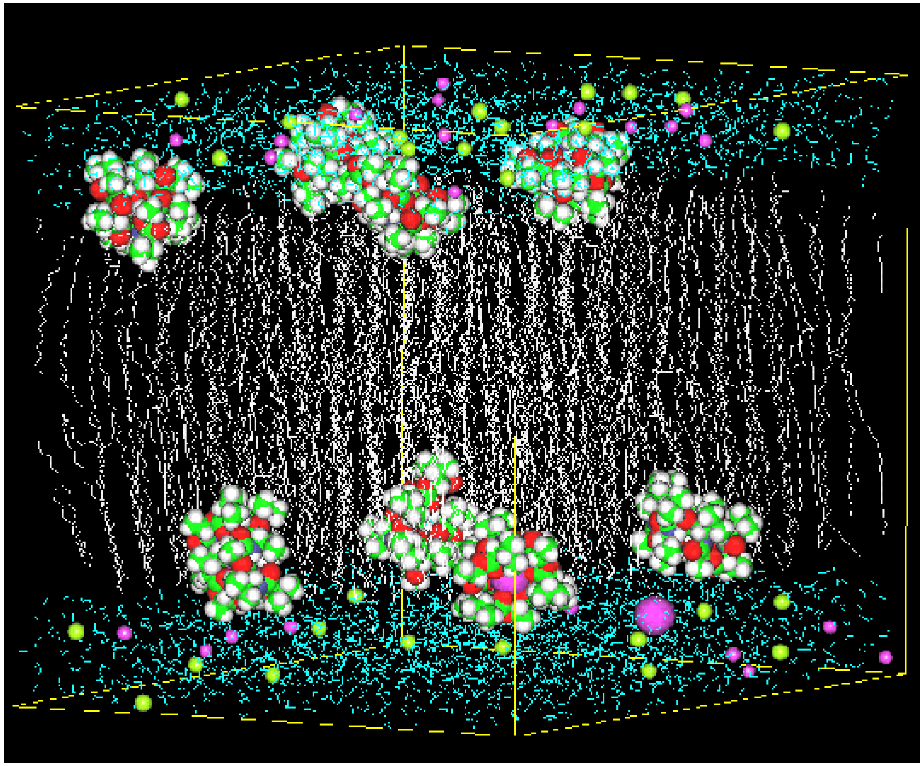
ΔG(ATP hydrolysis)= -43.1-49.1 kJ/mol

Valinomycin: Composed of D and L amino acids

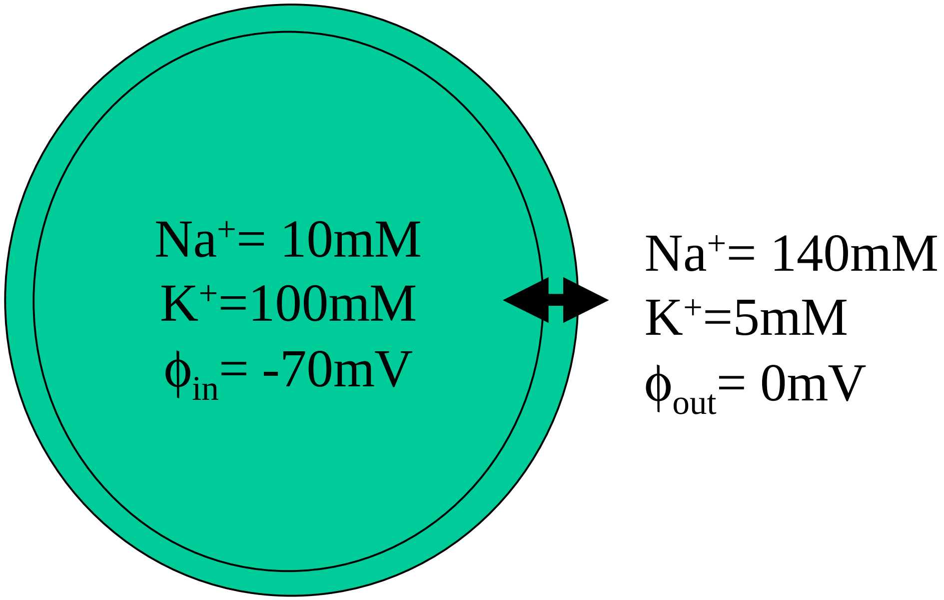
Hydrophobic exterior

Binds K^+ 1000X as strongly as Na^+ (Turnover rate is about 10^4 cations/sec)





Gramicidin ($2x10^7$/sec but nonspecific for a wide range of ions)



So if water could pass freely through the membrane (it can)…and I were to dump this cell into distilled/deionized water, what would happen?

We need to discuss colligative properties again.

Colligative Properties

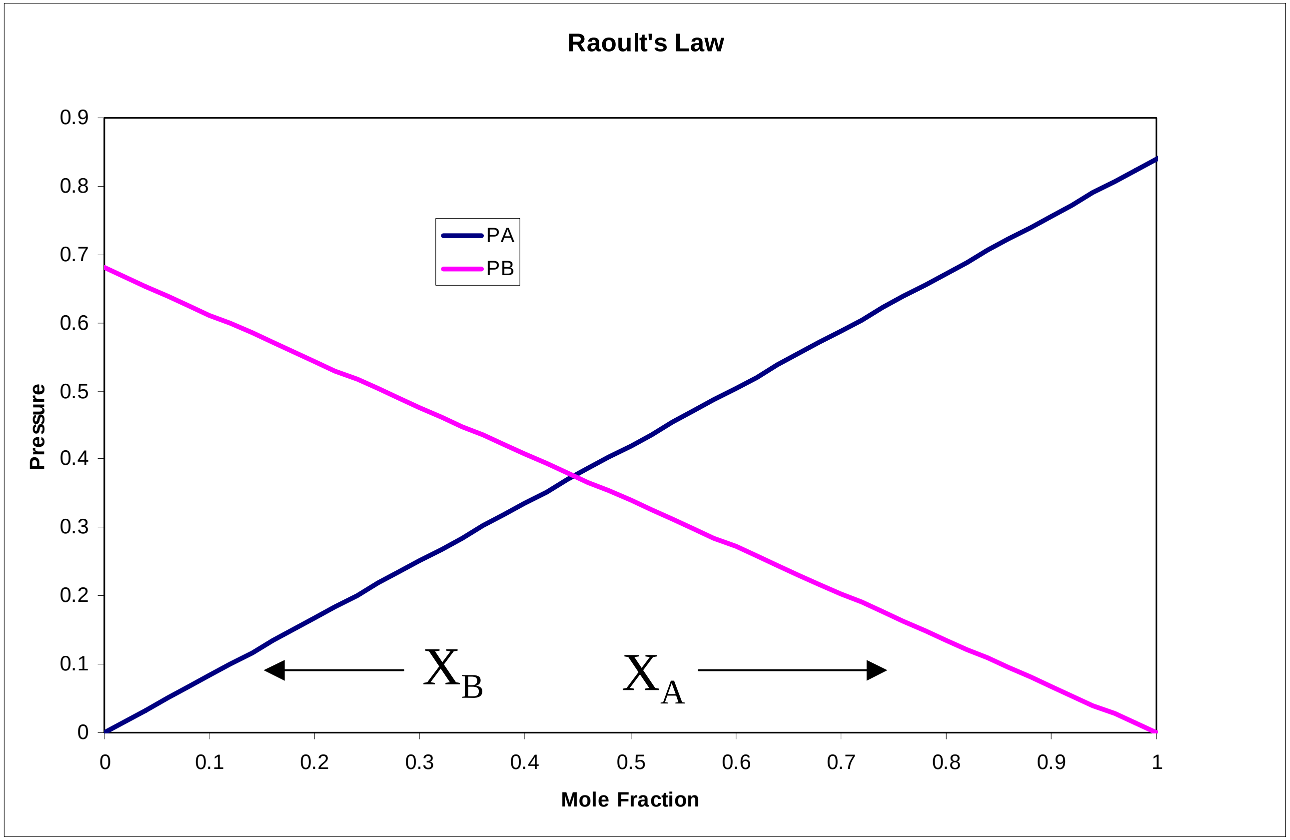
Colligative properties depend on the number of particles rather than their nature

- Lowering of the vapor pressure (Raoult’s law)
- Elevation of the boiling point (“ebulioscopy”)
- Depression of the freezing point (“cryoscopy”)
- Osmotic pressure

Raoult's law

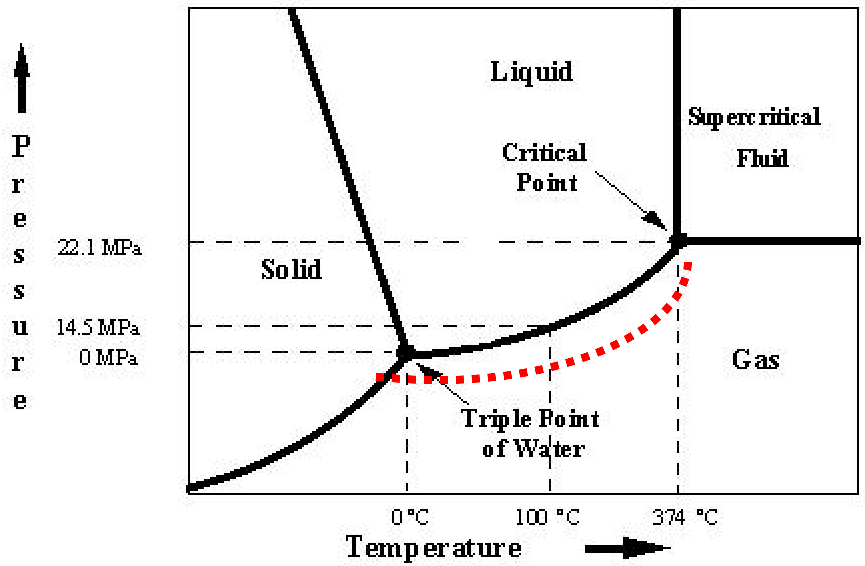
$$P_A = X_A P_A°$$

A graph of this property is given by



T-dependence of K and Phase Diagrams

Phase Diagram for Water

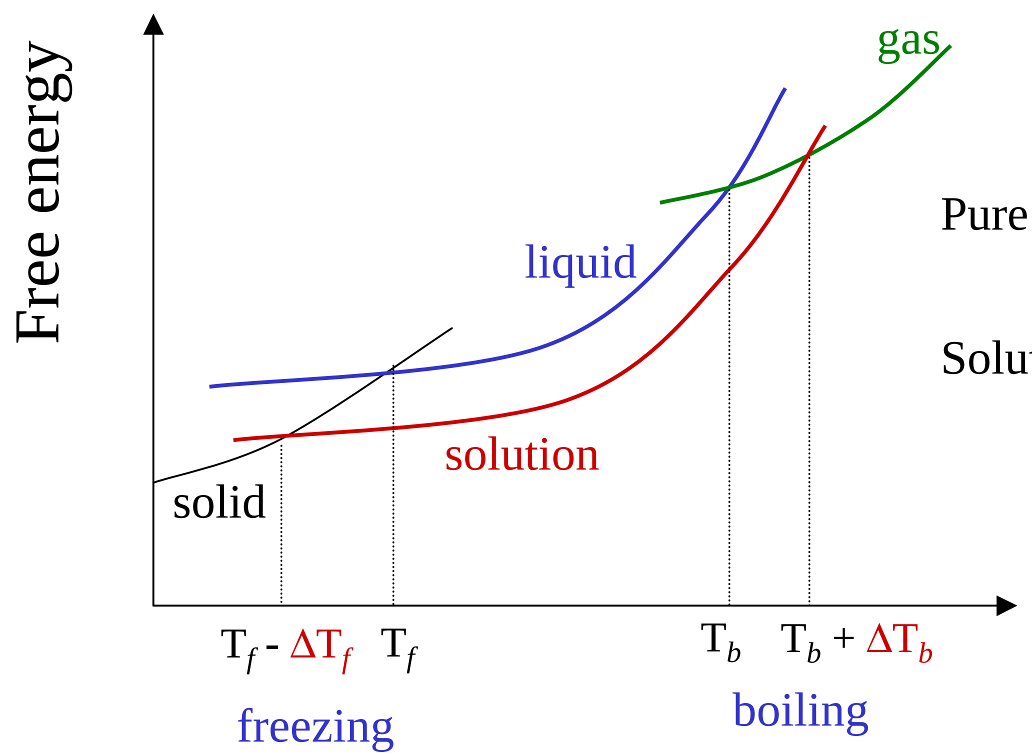


1atm= 101,325 Pa

The black lines are loci of point at which the two (or three) phases of water are in equilibrium.

On either side of the black lines, water enters the pure state.

Ebulioscopy and Cryoscopy



Pure solvent $\mu_w = \mu_w^o$

Solution $\mu_w = \mu_w^o + RT \ln x_w$

negative

Freezing point depression: ΔT_f

Boiling point elevation: ΔT_b

ΔTf and ΔTb

- Freezing point depression:

$$\Delta T_f = K_f \cdot c_{solute}(mole/L)$$

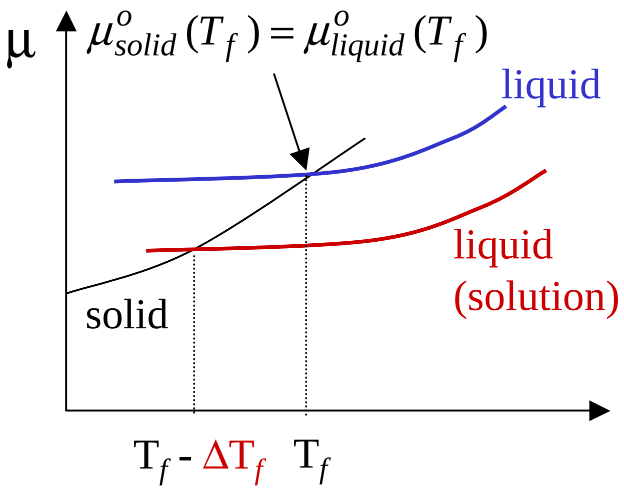
K_f - “cryoscopic constant” or “molar depression constant” {^{o}C/M}

- Boiling point elevation:

$$\Delta T_b = K_b \cdot c_{solute}(mole/L)$$

K_b - “ebulioscopic constant” or “molar elevation constant” {^{o}C/M}

Justification: ΔTf



In equilibrium at $T = T_f - \Delta T_f$:

$$\mu^o_{solid}(T_f - \Delta T_f) = \mu^o_{liquid}(T_f - \Delta T_f) + RT \ln x_{solvent}$$

$$RT \ln x_{solvent} = \mu^o_{solid}(T_f - \Delta T_f) - \mu^o_{liquid}(T_f - \Delta T_f)$$

$$\ln x_{solvent} = \ln(1 - x_{solute}) \approx -x_{solute} \quad (x_{solute} << 1)$$

$$\mu^o_{solid}(T_f - \Delta T_f) - \mu^o_{liquid}(T_f - \Delta T) =$$

$$= \mu^o_{solid}(T_f) - \frac{\partial \mu_{solid}}{\partial T}\Delta T_f - \mu^o_{liquid}(T_f) + \frac{\partial \mu_{liquid}}{\partial T}\Delta T_f$$

$$\frac{\partial \mu_{solid}}{\partial T} = -S^o_{solid} \quad \frac{\partial \mu_{liquid}}{\partial T} = -S^o_{liquid} \quad \mu^o_{solid}(T_f) - \mu^o_{liquid}(T_f) = 0 \quad T_f >> \Delta T_f \Rightarrow$$

$$RT_f x_{solute} \approx (S^o_{liquid} - S^o_{solid})\Delta T_f = \frac{(T_f S^o_{liquid} - T_f S^o_{solid})}{T_f}\Delta T_f = \frac{\Delta H_{melting}}{T_f}\Delta T_f \Rightarrow$$

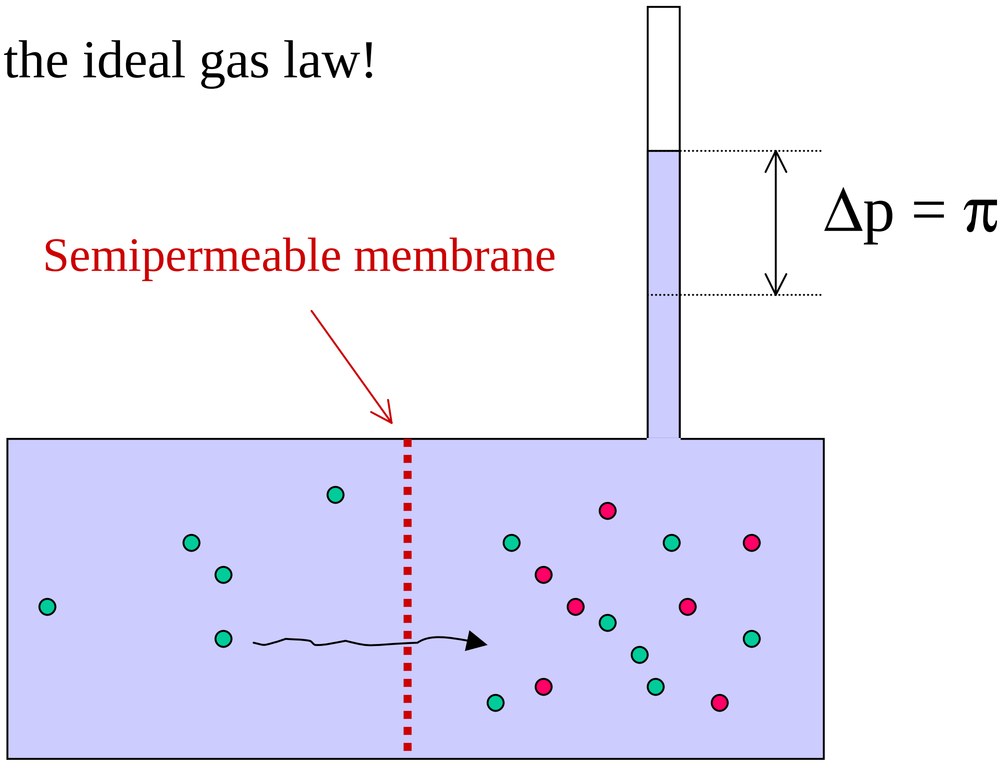
$$\boxed{x_{solute} \approx \frac{\Delta H_{melting}}{R{T_f}^2}\Delta T_f}$$

$$\boxed{\Delta T_f \approx \frac{1000 R{T_f}^2}{M_{solvent}\Delta H_{melting}}(= K_f)c_{solute}}$$

Osmotic Pressure

$$\boxed{\pi = RT \cdot c_{solute}}$$

It looks a little like the ideal gas law!



$$\mu_w = \mu_w^o \quad > \quad \mu_w = \mu_w^o + RT \ln x_w$$

Justification: Osmotic Pressure

For pure solvent:

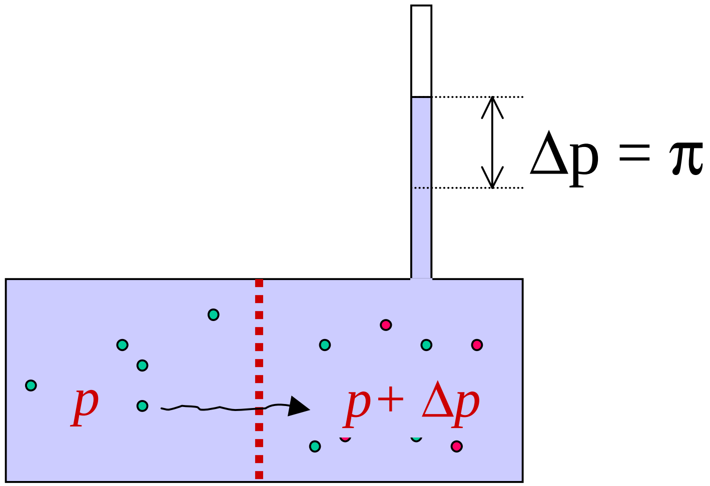
$$\mu(p) = \mu^o(p)$$

For the solution:

$$\mu(p+\Delta p) = \mu^o(p+\Delta p) + RT\ln x_{solvent}$$

$$\ln x_{solvent} = \ln(1 - x_{solute}) \approx -x_{solute} \qquad (x_{solute} << 1)$$

$$-RTx_{solute} = \mu^o(p+\Delta p) - \mu^o(p) = \frac{\partial \mu}{\partial p}\Delta p(=\pi)$$



Remembering that

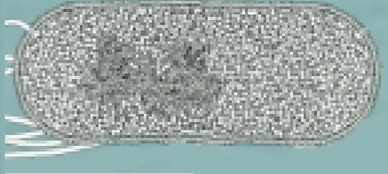
$$dG = Vdp$$

$$\Delta G = \int_{1+\pi}^{1} \overline{V}_x dP = -\overline{V}_x \pi$$

So

$$-x_{solute} = \frac{-\overline{V}_x \pi}{RT} = \frac{-n_b}{n_a + n_b}$$

$$\boxed{\pi = RT \cdot c_{solute}}$$



Osmosis is important!

A report in the **23 April 1998 issue of The New England Journal of Medicine** tells of the life-threatening complications that can be caused by an ignorance of osmosis.

- Large volumes of a solution of 5% human albumin are injected into people undergoing a procedure called plasmapheresis.

- The albumin is dissolved in physiological saline (0.9% NaCl) and is therefore isotonic to human plasma (the large protein molecules of albumin have only a small osmotic effect).

- If 5% solutions are unavailable, pharmacists may substitute a proper dilution of a 25% albumin solution. Mixing 1 part of the 25% solution with 4 parts of diluent results in the correct 5% solution of albumin. BUT, in several cases, the diluent used was sterile water, not physiological saline. SO, the resulting solution was strongly hypotonic to human plasma.

- **The Result: massive, life-threatening hemolysis in the patients.**

Molecular Weight Determination

$$c_{solute}(mole/L) = \frac{n_{solute}}{V} = \frac{m_{solute}/M_{solute}}{V} = \frac{c'(g/L)}{M_{solute}}$$

- Osmotic Pressure:

$$M_{solute} = \frac{c'_{solute}(g/L)}{\pi}RT$$

- Cryoscopy and Ebulioscopy:

$$M_{solute} = \frac{c'_{solute}(g/L)}{\Delta T_f}K_f \qquad M_{solute} = \frac{c'_{solute}(g/L)}{\Delta T_b}K_b$$

Homework:

TSW 5.3(b,c),5.4,5.10,5.12,5.19,5.30